LANGMUIR DIBLOCK COPOLYMER MONOLAYERS

STUDY OF TETHERED POLYMER BRUSHES

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Abstract

The molecular weight dependence of segmental concentration profile of langmuir monolayers of poly(dimethyl siloxane)-*b*-polystyrene (PDMS-*b*-PS) diblock copolymers on dioctyl phthalate (DOP) in theta solvent conditions will be investigated using NG7 horizontal neutron reflectometer. The aim of this measurement is to provide hands on experience in data collection, reduction and analysis for neutron reflectivity measurements of liquids.

1.Introduction

Polymer Brushes (Tethered Chains)

Polymer brushes are formed by tethering an ensemble of polymer chains to a surface such that each chain has one end covalently bound to the surface and the tethering points are sufficiently close together that the chains must stretch appreciably away from the Gaussian coil configurations preferred in a melt of untethered chains.[1]

When polymer chains are tethered to a surface, two cases can be distinguished depending on the grafting density (σ). In the first case, the distance between two anchored polymers is greater than the radius of gyration (R_g) of the unperturbed chain so that the segments of distinct polymer chains do not interact with each other.[2] When there is a weak or repulsive interaction between the polymer chains and the surface, the polymer chains are attached to the surface through a short stem and form a typical random coil, yielding a "mushroom" conformation. The degree of chain overlap can be compared for chains of different molecular weight using a reduced surface density, $\Sigma = \sigma\pi R_g^2$, where R_g is the radius of gyration of a free chain in dilute solution. Mushroom regime covers the range of $\Sigma = 0$ -4 and the thickness of polymer chains are scaled with σ^0 (Figure 1). The overcrowding of tethered polymer chains in solution starts around $\Sigma \sim 4$ and it is not clear at which Σ value chains become strongly stretched.[3] It has been shown that even for $\Sigma \sim 12$, the strongly stretched brushes were not obtained.

A completely different picture can be obtained when the polymer chains are attached to the surface at high grafting densities. Dense grafting of polymer chains on an interface enforces a strong overlap among the coils, increases the segment-segment interactions and the corresponding interaction energy. In this case, polymer chains avoid each other to minimize segment-segment interactions by stretching away from the surface. In strongly stretched brush regime, the thickness scales with $\sigma^{1/3}$. Stretching of polymer chains decreases the number of possible polymer conformations and hence the configurational entropy of the polymer chains. The deformation of tethered polymer chains reflects a balance between enthalpic interaction and elastic free energies. Stretching lowers the interaction energy per chain, F_{int}, at the expense of a high elastic free energy, F_{el}. Stretching and retraction forces establish a new equilibrium at a higher energy level in which the chains are stretched perpendicular to the surface.

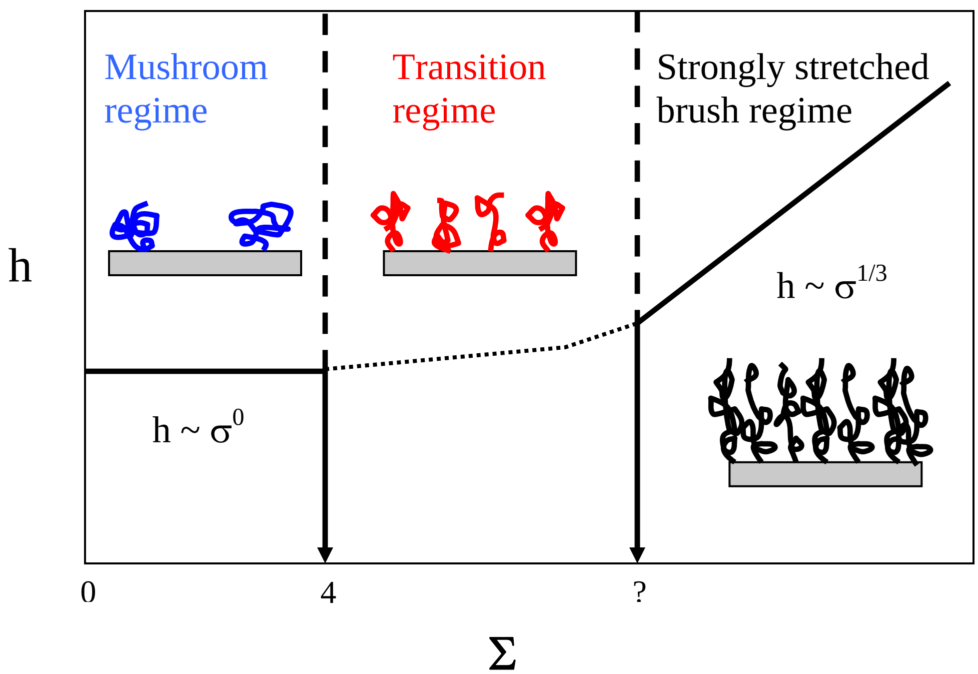

Figure 1. Schematic representation of the thickness of tethered chains on a substrate in solution versus Σ. The Σ~ 1 is the reference point at which tethered chains starts to laterally interact with each other. Note that the tethered chains start to get squeezed by their neighbors at Σ ~ 4.

Polymer brushes are model systems for many practical polymer systems such as block copolymers and graft copolymers at fluid-fluid interfaces, and polymer micelles. They are also of interest due to their potential practical uses to control adhesion, lubrication, or wetting properties of surfaces, flocculation in colloidal dispersions, solvent flow through channels, and to create protein and cell-resistant biosurfaces.[1] Polymer brushes are very attractive in surface modification since thin polymer films created by covalent attachment of polymer chains to a substrate have very strong resistance against various solvents and high temperature.

Initial theoretical work using scaling arguments and analytical self-consistent field (SCF) calculations are valid in the limit of infinite molecular weight (M) and high σ. This regime is the strongly stretched brush regime. Both scaling and SCF approaches yield the same scaling dependencies on σ and M such that the layer height (h) varies as $h \sim \sigma^{1/3}M$ in good solvent and $h \sim \sigma^{1/2}M$ in theta solvent. When the tethered chains are formed from dilute solutions, they fall into the transition category between mushroom and strongly stretched brush regimes. It is important to check the validity of scaling laws for tethered chains in this transition regime.

There are numerical SCF calculations, Monte Carlo and molecular dynamics (MD) simulations that investigate the structure of tethered chains in transition regime. They provide detailed segmental profile of brushes which shows a depletion of segments from the surface region when the chains are tethered to a non-interacting hard wall. The depletion layer is formed due to restrictions on the conformations of chains residing adjacent to an impenetrable surface. Numerical SCF and MD simulations predicted that the depletion layer increases with M and is independent of σ, whereas earlier scaling studies predicted that the depletion layer is independent of M and decreases with σ. One objective of this experiment is to investigate how depletion layer varies with M.

Tethering Approach

For this experiment, polymer brushes will be created using Langmuir monolayers of highly asymmetric poly(dimethyl siloxane)-*b*-polystyrene (PDMS-*b*-PS) diblock copolymers on the surface of an organic solvent as shown in Figure 2.[4,5] The surface tension values of PDMS, PS and dioctyl phthalate (DOP) at room temperature are 20, 40 and 31 mN/m, consecutively. The PDMS block anchors the copolymer to the surface and PS block extend into the organic solvent. The anchoring energy is determined by the magnitude of the surface tension of DOP relative to the surface tension of PDMS block. The nature of the interaction between the air surface and PS block is determined by the surface tension of DOP relative to surface tension of PS. Polymer blocks are very strongly attached to the liquid/air interface due to low surface tension of PDMS block relative to DOP. In this system, the air surface is repulsive for PS block.

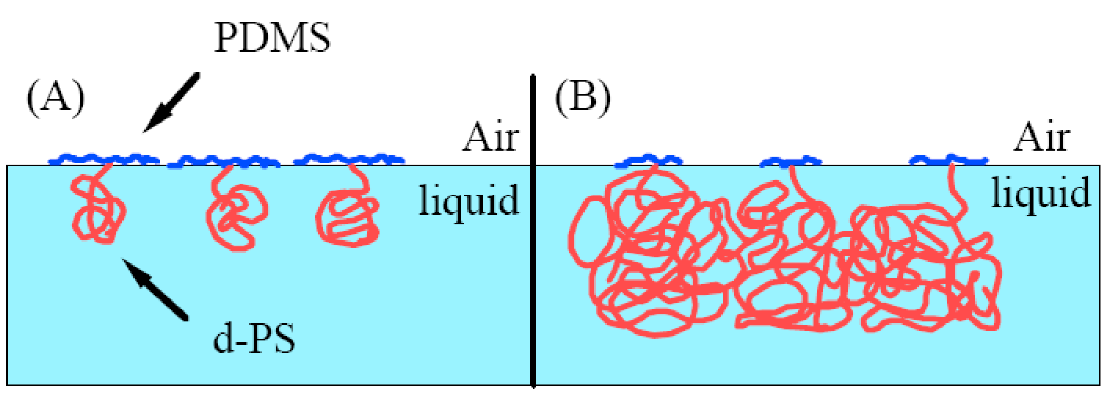

Figure 2. Illustration of Langmuir diblock copolymer monolayer system formed by PDMS-PS on an organic liquid. (A) symmetric copolymers, (B) asymmetric copolymers (N_{PS}>>N_{PDMS})

2. Experimental

2.1. Materials

- PDMS-*b*-PS diblock copolymers that have four different molecular weights. PS block is fully deuterated.

- DOP is a theta solvent for PS at 22 °C.

- Chloroform

2.2. Procedure

The Langmuir monolayers will be spread from a solution of diblock copolymer in chloroform using a microsyringe onto DOP which was maintained at 22 °C. The interfacial tension will be measured using Wilhelmy plate technique. Tensiometer will be removed and sample will be aligned in neutron beam. Neutron reflectivity measurement will be performed overnight and the collected data will be analyzed by fitting to three different functional forms.

2.3. NG7 Horizontal Neutron Reflectometer

Reflectivity measurements will be performed on the NG7 horizontal reflectometer. Liquid-air interfaces can only be measured using a horizontal geometry reflectometer. NG7 uses a fixed wavelength of 4.75 Å. The schematic of NG7 is shown in Figure 3. A tilting pyrolytic graphite monochromator is located at the bottom 1cm of guide NG7. The resulting beam profile is approximately 50mm in width with a maximum height of 10mm. The reflectometer is designed for incident wavelengths λ=2.35, 4.1, 4.75, 5.5Å. The beam is filtered against thermal neutrons after the monochromator with either a graphite filter for λ =2.35Å or a liquid nitrogen cooled beryllium filter for λ >4Å. The neutron flight tubes have $2\theta c$ super mirrors mounted on their vertical surfaces to reduce losses due to horizontal beam divergence. All flight tubes have single crystal sapphire windows and are evacuated to reduce losses from air scattering. The pre- and post-sample flight paths are 2m in length and each has a pair of independently controlled LiF slits for collimation of the incident or scattered beam. Horizontal collimation is also available before and after the sample position. A beam monitor detector located after the second collimating slit samples a portion of the beam incident on the sample and allows the primary detector data to be scaled to absolute reflectivities. The instrument has two available detectors: (1) a 2.5cm diameter cylindrical 3He proportional counter which is used with the final set of collimating slits, or (2) an ORDELLA linear position sensitive 3He proportional counter with a 10cm position-sensitive length and a 4 cm width. The detector is used without the final set of collimation slits.

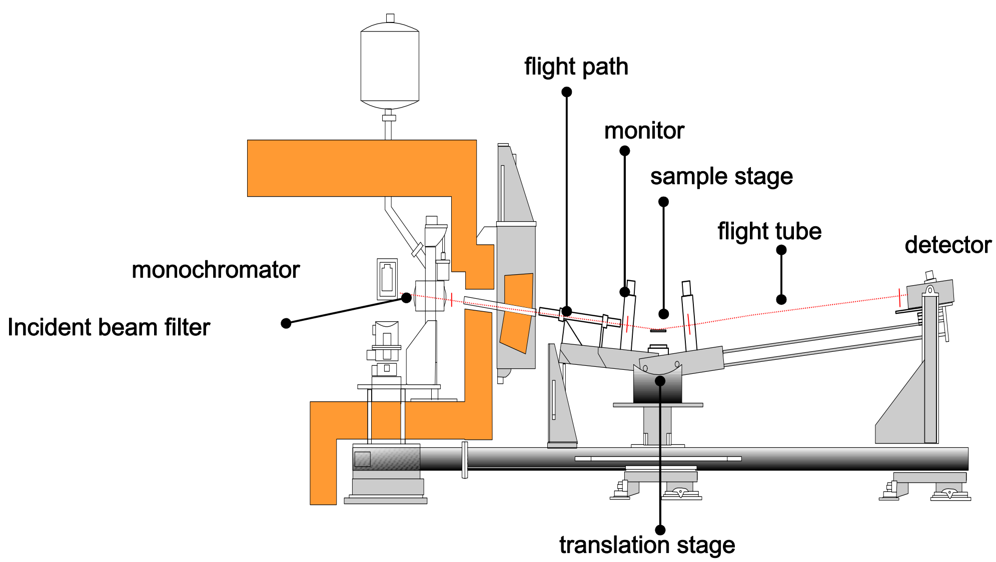

Figure 3. Schematics of NG7 horizontal neutron reflectometer.

The only way to measure a segmental density profile for this system is to do a neutron reflectivity measurement. The neutron scattering length density of hydrogenous PDMS block is nearly matched with that of air so only the submerged deuterated PS block contributes to the reflectivity.

3. Objectives of the experiment

The objectives of this experiment are

a) To determine the segmental density profile of polymer brushes in transition regime

b) To check the validity of scaling laws derived for strong stretching regime in the transition regime

c) To determine the effect of molecular weight on the depletion layer

d) To learn reflectivity measurements for liquid-air interfaces and have fun

References

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